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PHASE COMPOSITION AND MORPHOLOGY OF PRODUCTS OF COMBUSTION OF FERROSILICON IN NITROGEN

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The results of a study of silicon nitride phase formation in combustion of ferrosilicon in gaseous nitrogen are reported. It was shown that formation of α - or β -modifications of silicon nitride is basically determined by the composition of the batch for self-propagating high-temperature synthesis. When ammonium chloride was added to the initial ferrosilicon, a combustion product with a high (up to 80%) α - Si_3N_4 content is formed, while dilution with the final product and magnesium fluoride results in predominant (more than 95%) formation of β - Si_3N_4 . The particle size and shape are a function of the conditions of synthesis and are primarily determined by the temperature and the additives incorporated in the initial alloy.

Silicon nitride, which has unique performance properties (high strength, crack resistance, resistance to high-temperature oxidation, corrosion resistance in aggressive media, heat resistance, etc.), is increasingly widely used in modern technology. Furnace synthesis and plasma chemical methods are the basic industrial methods of manufacturing silicon nitride. These methods are distinguished by high energy capacity and the use of expensive equipment and initial materials, which is reflected in the cost of the silicon nitride powders obtained with these technologies.

The method of self-propagating high-temperature synthesis (SHS), which allows attaining high reproducibility with minimum power consumption since no external sources of heat are used, occupies a special position. The SHS method does not introduce contaminants in the synthesis process, so that the purity of the product is determined by the purity of the initial silicon. To obtain pure silicon nitride powders by the SHS method, silicon wastes of semiconductor purity are used as the raw material [1, 2]. The combustion products are in the form of cake and must be ground. One available method of dispersing the powders is still grinding in a mill with steel balls, but the silicon nitride is contaminated with iron, and chemical treatment in hydrochloric acid solutions is required to remove it.

We showed (RF Patent No. 2257338) [3] that silicon nitride can be obtained from ferrosilicon, which is manufactured by domestic industry in large amounts, since it is used

as a hardener and scavenger in smelting steel. Ferrosilicon is a brittle material, and when ground, it forms a large amount of fine fraction (dust) which is removed by the ventilation system and is finished feedstock for high-temperature synthesis of silicon nitride. The product of combustion of ferrosilicon in nitrogen is a composite of silicon nitride and iron. After acid concentration in hydrochloric acid solutions, silicon nitride powder with a 0.05% residual iron content is obtained.²

The results of a study of the effect of the basic synthesis parameters on the phase composition and morphology of silicon nitride particles are reported.

PUD-75 powdered ferrosilicon wastes — polydisperse powder with a particle size less than 160 μm and 79.0% silicon content — was used as feedstock. According to the results of x-ray phase analysis, the alloy was a two-phase material consisting of silicon and high-temperature lebeaultite FeSi_2 . The ferrosilicon powder was poured in cylindrical metal mesh tubes 38 – 60 mm in diameter. The samples were burned in a constant-pressure unit in an atmosphere of nitrogen. The nitrogen pressure varied from 1 to 10 MPa. The samples were ignited from the powdered igniting mixture with a tungsten coil through which an electric current was passed. After passage of the combustion front, the sample was held in nitrogen until totally cooled, then the pressure was released and the product of SHS was removed from the unit for further investigation.

The x-ray phase analysis was conducted on a DRON-2 diffractometer using Co radiation. The electron-microscopic

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² Here and below: mass content.

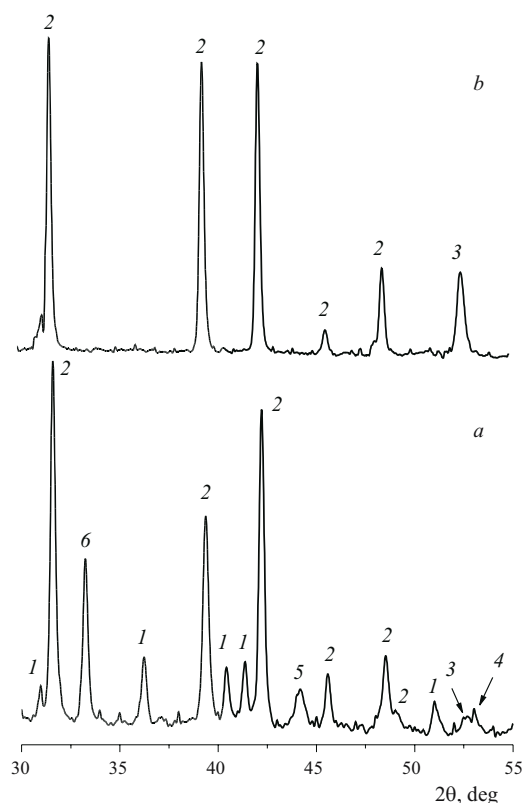


Fig. 1. Fragments of x-ray patterns of products of combustion of ferrosilicon in nitrogen with no additives (*a*) and with 60% previously nitrated ferrosilicon (*b*): 1) α - Si_3N_4 ; 2) β - Si_3N_4 ; 3) Fe; 4) FeSi; 5) FeSi_2 ; 6) Si.

microdiffraction analysis of the materials by transillumination (TEM) was conducted on an ÉM-125 instrument. The morphology of the initial and synthesized powders was investigated with a JEM-100CXII electron microscope with an ASID-4D scanning attachment (JEOL, Japan). The combustion temperature was measured with a tungsten-rhenium thermocouple (BP5-BP20) 100 μm in diameter placed in the sample at a depth of 15 mm.

The presence of two crystalline modifications α - and β - Si_3N_4 is characteristic of silicon nitride. Both modifications have a hexagonal crystal lattice with parameters: $a = 0.776$ nm, $c = 0.5662$ nm, and $a = 0.7603$ nm, $c = 0.2907$ nm, respectively [4]. A monotropic transition of the low-temperature α -modification into the high-temperature β -phase was observed with an increase in the temperature [5]. According to the developed concepts, it is preferable to use initial silicon nitride powders with a high content of the α -modification for fabricating dense ceramic materials, since the $\alpha \rightarrow \beta$ transition that takes place in hot molding strengthens the ceramic material.

The products of the reaction of ferrosilicon with nitrogen (according to XPA data) were usually primarily the β -modification with a small amount (under 20%) of α - Si_3N_4 . In addition

to the basic phases, free silicon, iron, and iron silicides FeSi_2 , FeSi , Fe_5Si_3 , and Fe_3Si were also found in the sample, and their presence indicates incomplete nitride formation.

The change in such synthesis parameters as the initial nitrogen pressure, batch density, dispersion of the initial powder, and sample diameter did not result in total conversion of silicon into nitride. The products of combustion of ferrosilicon in nitrogen are multiphase. The multiphasicity of the combustion products is due to melting of the ferrosilicon, coagulation of drops of the iron-silicon melt, and formation of reaction cells which are several times larger than the particle size of the initial ferrosilicon (RF Patent No. 2257338).

To eliminate coagulation processes, a high-melting component — previously synthesized silicon nitride — or previously nitrated ferrosilicon with a low (approximately 0.7) degree of nitriding (the maximum degree of nitriding is the ratio of the amount of nitrogen absorbed by the sample during synthesis to the amount of nitrogen required for total conversion of silicon into nitride) was added to the initial batch to eliminate coagulation processes. Regardless of the silicon nitride modification added to the initial batch, only the high-temperature β -modification was always present in the combustion products in this case (Fig. 1). This is because the effect of coagulation inhibition of the reaction was eliminated on addition of the high-melting component, and consequently the maximum possible degree of nitriding was attained. The maximum temperature in the reaction zone, measured by the thermocouple method, was 2100°C. The high synthesis temperature determined the mechanism of silicon nitride crystal growth (vapor – liquid – crystal [6]) and fostered formation of acicular and lamellar crystals (Fig. 2). Large crystals with a cubic crystallographic face were the high-temperature β -modification of silicon nitride.

Addition of magnesium fluoride (1.0%) to the initial ferrosilicon allowed attaining the maximum degree of nitriding and obtain the composite mixture $\text{Fe} - \text{Si}_3\text{N}_4$. The studies showed that addition of magnesium fluoride primarily intensified nitriding of iron silicides, completed by formation of silicon nitride and liberation of iron. The results of the x-ray phase analysis of the combustion products show that primarily β - Si_3N_4 (95%) was formed in the presence of magnesium fluoride. Even at low pressures, where the combustion temperatures are low, the α - Si_3N_4 content did not exceed 5%. When magnesium fluoride was added to the initial ferrosilicon, whisker-like silicon nitride crystals were formed (see Fig. 2).

Addition of ammonium chloride (1 – 10%) to the initial ferrosilicon led to a combustion product with a different ratio of α - and β -modifications of silicon nitride. By varying the initial nitrogen pressure and amount of ammonium chloride, nitrated ferrosilicon with both 100% β - Si_3N_4 and with a high α - Si_3N_4 content (up to 80%) can be synthesized. The x-ray pattern of nitrated ferrosilicon burned in the presence of 7% ammonium chloride at a pressure of 7 MPa is shown in

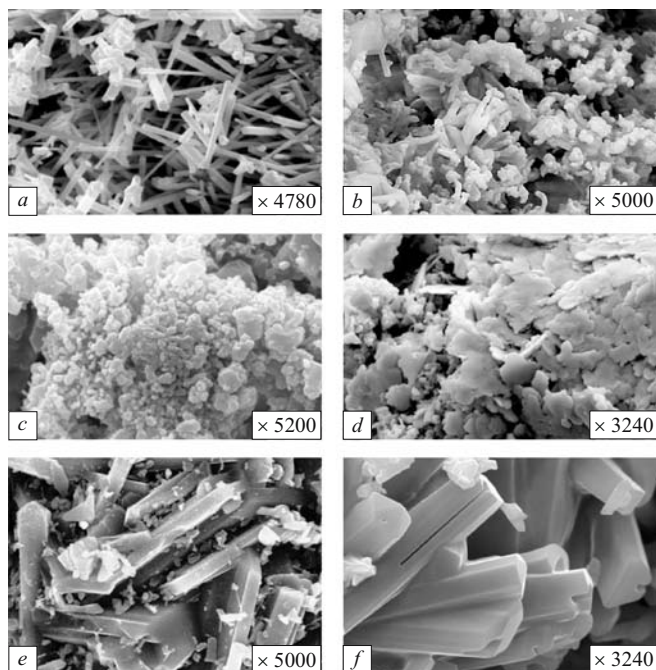


Fig. 2. Morphology of silicon nitride particles formed in combustion of ferrosilicon in nitrogen in the presence of magnesium fluoride (a), ammonium chloride (b – d), and in dilution with previously nitrated ferrosilicon (e, f).

Fig. 3. The α - Si_3N_4 content in it, calculated with the intensity of the peaks in the x-ray pattern, was 75%.

Based on the data from a thermodynamic calculation performed with Astra-4 software developed at the Bauman Moscow State Technical University [7], the equilibrium composition of the gaseous products is represented by the following components: HCl , H_2 , SiCl_2 , FeCl_2 , N_2 , H , Cl_2 , NH_3 , Si_2 , SiH_2 , SiCl , SiCl_4 , FeCl , NH , Si , SiH_3 , SiHCl , Cl , NH_2 , Si , SiH , SiH_4 , SiCl_3 , Sn , Fe , FeCl_3 , and Fe_2Cl_4 . The variety of gaseous products suggests that a significant part of the reactions takes place in the vapor-gas phase in the presence of ammonium chloride.

According to the results in [8], silicon nitride is formed in the presence of ammonium chloride through intermediate compounds — silicon tetrachloride and diimide. Nitriding of ferrosilicon with formation of intermediate products (SiCl_4 , $\text{Si}(\text{NH})_2$) is a complex multistage process that is reflected in its kinetic characteristics. The combustion rate decreases with an increase in the ammonium chloride, and this can stop combustion in the self-propagating regime due to perceptible heat losses. Addition of ammonium chloride thus reduces both the combustion rate and the temperature, as the appearance of the low-temperature α -modification of silicon nitride in the combustion products indicates.

Since nitriding reactions basically take place in the gas phase in the presence of ammonium chloride, the silicon nitride particles obtained are much smaller than in dilution of the initial melt with nitrated ferrosilicon and are individual

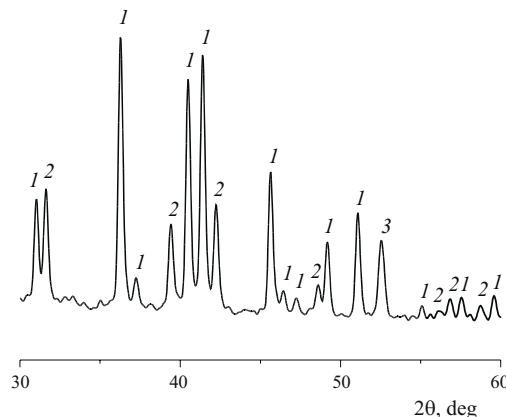


Fig. 3. Fragment of the x-ray pattern of nitrated ferrosilicon with addition of 7% NH_4Cl : 1) α - Si_3N_4 ; 2) β - Si_3N_4 ; 3) Fe .

isometric and columnar crystals, as well as shapeless formations (see Fig. 2).

The study of the effect of the conditions of synthesis on the phase composition of the combustion products thus showed that the $\text{Si}_3\text{N}_4 + \text{Fe}$ composite can only be synthesized when ammonium chloride or magnesium fluoride is added and the initial melt is diluted with previously nitrated ferrosilicon. When MgF_2 is used as the additive and previously nitrated ferrosilicon is used, β - Si_3N_4 predominates in the product of synthesis (more than 95%). Synthesis of silicon nitride with a high content (up to 80%) of the low-temperature α -modification is only possible in the presence of ammonium chloride.

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